Polydiacetylene Thin Films for Photonic Applications

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The goal of this work is to study the process of photodepositing polydiacetylene films onto transparent substrates from monomer solutions by irradiation with ultraviolet light. The process is a novel technique for the formation of thin amorphous films useful in nonlinear optical devices. Further, the process involves gravitational effects during photopolymerization—heretofore unreported in the literature. This work represents the extension of an earlier funded Research and Technology Operating Plan.

Polydiacetylenes are an extremely promising class of polymers for such photonic applications as wave-guiding and nonlinear optics.[1,2] Because of their highly conjugated electronic structures, they can have large, nonlinear optical coefficients with very fast response times, rendering them useful for applications such as ultra-fast, all-optical switching. Researchers have continued, through various discretionary funding sources, to conduct ground-based research on polydiacetylenes, as well as other organic and polymeric nonlinear optical materials. As a result, a simple, novel technique for the formation of thin amorphous films of a polydiacetylene (PDAMNA) derived from 2-methyl-4-nitroaniline was discovered and developed here at MSFC (patent pending). [3,4]

It is well known that such gravitational effects as buoyancy-driven convection can affect solution processes.[5] Evidence of this is seen in the photodeposition of PDAMNA thin films from solution: films grown in one-gravity contain small (submicron) solid particles embedded throughout them. These particles consist of precipitated polymer that forms in the bulk solution as polymer chains grow and eventually exceed their solubility. Thermal convection, induced by uneven heat generation in the solution from the ultraviolet radiation, transports the particles to the surface of the growing film, where they become embedded. These particles are defects that can scatter light, thereby lowering the optical quality of the films.

The objective of this work is to study photodepositing polydiacetylene films onto transparent substrates and the accompanying gravitational influences on film quality and morphology. By irradiating only part of the substrate with ultraviolet light, films can be obtained in desired patterns; a laser can even be used to form polymeric circuits. By varying the orientation of the growth chamber with respect to gravity to minimize convection, the concentration of particles in the films can be reduced but not eliminated. Additionally, there is some evidence to suggest that convection can have a detrimental effect on molecular orientation in thin films. This is important because well-ordered films are capable of significantly greater optical nonlinearities than poorly ordered films. The turbulent molecular motions that take place during convection can cause the growing polymer chains to become entangled and matted around each other, thus disrupting any natural ordering that might otherwise occur. Researchers assess that a convection model for the most gravitationally stable orientation in one-gravity is one of an unstable layer atop a stable layer, with penetrative convection. An experiment has been scheduled to fly on CONCAP IV [CONsortium Complex Autonomous Payload] aboard STS–69 (Fall 1995) to photodeposit PDAMNA thin films.

Researchers have been investigating the use of liquid crystal moieties chemically incorporated into the structure of PDAMNA to aid in inducing self-alignment of the polymer chains,[6] and have recently synthesized a modification of the diacetylene monomer that appears to exhibit the desired liquid crystalline behavior. Pre-ordered substrates are being used as templates upon which to carry out photodeposition in hopes of achieving quasiepitaxial film growth.

The reduced convection environment of microgravity could be a significant asset to achieving molecular orientation in these films. Further, scattering losses in these promising nonlinear optical films could be markedly minimized, leading to benchmark devices. Among the most important assets to this research are the discoveries of a new process for depositing thin films with good optical quality, and a heretofore unexplored mechanism leading to convection affecting thin-film growth.

Photopolymerization in solution seems to be a gravitationally sensitive process. Observed variations in film quality due to reaction-cell orientations relative to the gravity vector raise some interesting opportunities for microgravity research. Fundamental science questions will be answered through microgravity processing, with probable technological advances through benchmark device fabrication on orbit.

[1]*Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 2. 1987. Chemla, D.S., and Zyss, J., eds. Academic Press: Orlando, Florida.

[2]Prasad, P.N., and Williams, D.J. 1991. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*. John Wiley and Sons, Inc.: New York.

[3]Paley, M.S.; Frazier, D.O.; Abdeldeyem, H.; and McManus, S.P. 1994. *Chemistry in Materials,* 6(12):2,213.

[4]Paley, M.S.; Frazier, D.O.; Abdeldeyem, H.; Armstrong, S.; and McManus, S.P. 1995. *Journal of the American Chemical Society,* 117(17):4,775.

[5]*Fluid Sciences and Materials Science in Space*. 1987. Waler, H.U., ed. Springer-Verlag: New York.

[6]*Side-Chain Liquid Crystal Polymers.* 1989. McArdle, C.B., ed. Chapman and Hall: New York.

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